On the Conductivity of Salt Vapours.

By S. J. KALANDYK.

It has been shown by Beattie,[*] Garrett,[†] and Garrett and Willows,[‡] that when certain salts are heated up to 300–400° C. one can observe the discharge of positive and negative electricity. This phenomenon is observed more particularly in the case of the halogen salts of cadmium, zinc and ammonium. The researches of Schmidt[§] and Sheard[||] have shown that the discharge is due to two factors, (1) emission of the charges from the surface of the heated salt, and (2) to the conductivity of the salt vapours themselves. The thermionic effect of the above-mentioned salts was studied in detail by Prof. O. W. Richardson[¶] and his pupils, while some investigations of the electrical properties of the salt vapours were made by Schmidt in the papers referred to above. The object of the present research was to investigate the influence of the temperature, water vapour, time, etc., on the current passing in the salt vapours.

The Thermionic Effect of the Salt and the Conductivity of the Salt Vapours.

Some experiments were carried out in order to test whether the conductivity of vapours is due to charges which have diffused to other parts of the apparatus from the surface of the heated salt. For this purpose the vapours were investigated after passing through a cylindrical condenser in which the electric force was strong enough to sweep all charged particles to the electrodes. The apparatus used consisted of a small bulb A (fig. 1), in which the cadmium iodide was placed. The vapour at first passed through the plug of glass wool B to stop the large ions which might be produced during the heating of salt, then entered the condenser K_1, where the smaller ions could be removed by the electric field. The outer coating of the condenser K_1 was obtained by platinising the inner surface of the glass tube with a "liquid platinum" (from Deutsche Gold und Silber Scheide Anstalt) and was connected to earth. As the inner coating of the

* Beattie, 'Phil. Mag.,' vol. 48, p. 97 (1899).

† Garrett, 'Phil. Mag.,' (6), vol. 13, p. 728 (1907).

‡ Garrett and Willows, 'Phil. Mag.,' (6), vol. 8, p. 437 (1904).

§ Schmidt, 'Ann. d. Physik,' (4), vol. 35, p. 401 (1911), and (4), vol. 41, p. 673 (1913).

|| Sheard, 'Phil. Mag.,' (6), vol. 25, p. 370 (1913).

¶ O. W. Richardson, 'Phil. Mag.,' (6), vol. 26, p. 452 (1913).

condenser a glass rod covered with the same substance was used, and was connected by a platinum wire with the source of electromotive force.

For measuring the ionisation of the vapours a second cylindrical condenser K_2 was used. It consisted of an outer earthed platinum tube about 10 cm. long, in the axis of which a short platinum tube was fixed, the latter being connected to a gold leaf electroscope. Preliminary experiments were first made in order to test the action of the condenser K_1. For this purpose the bulb A was replaced by an open tube in which was placed a fine platinum strip which could be heated by an electric current. The tube D was connected with a water pump, and thus a stream of air was obtained which carried the ions emitted by the hot platinum upwards. When the electroscope was charged up to $+200$ volts, and both coatings of the condenser K_1 were earthed, it was found that the potential of the leaf fell 2 volts in five seconds. It required, however, about 90 seconds to fall the same amount when the inner surface of the condenser K_1 was charged up to ± 200 volts. It follows, therefore, that by this arrangement it is possible to stop practically all the ions entering the condenser K_1.

To test if the ionisation observed in the salt vapours is due to the surface effect, the bulb A was filled with 5 grm. of cadmium iodide, the whole apparatus was exhausted by cooled charcoal to the pressure 10^{-3} mm. of mercury and heated in the electric furnace to 298° C. When the current in the upper condenser became constant the inner surface of the condenser K_1 was charged up to 200 volts as in the previous experiment, and the current in the condenser K_2 was measured during about 15 minutes. The

Fig. 1.

difference between the readings with and without K_1 charged did not exceed the error of the experiment. Therefore we may conclude that the ionisation observed in the vapours is mostly due to the process which is going on in the vapours themselves, and is practically independent of the emission of charges from the surface of the heated salt. It may be remarked that Sheard (*loc. cit.*), working with apparatus of different construction, came to the same conclusion.
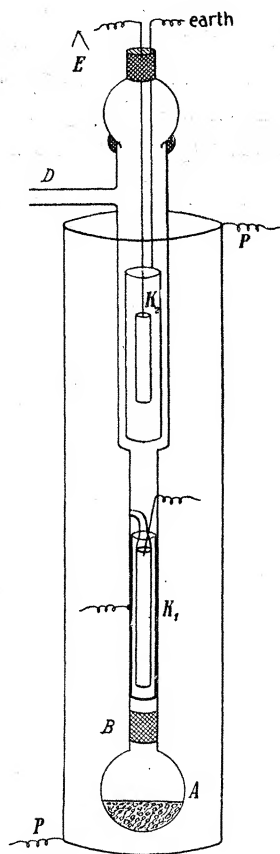
Influence of Water Vapour.

The influence of water on the conductivity of salt vapours has been studied by various experimenters, but the question is not yet definitely settled. Garrett, in the paper referred to above, noticed that when carefully dried zinc iodide was heated, no leak was observed; he therefore came to the conclusion that, in the case of this salt, water vapour is necessary for the production of ionisation. Quite recently Dr. Willows[*] again called attention to this point. Schmidt (*loc. cit.*), however, observed no difference between the conductivity of salt vapours in dry air and in the air which had been passed over boiling water.

To decide this important question the influence of water on the conductivity of salt vapours was studied in the following apparatus (fig. 2). The vapours
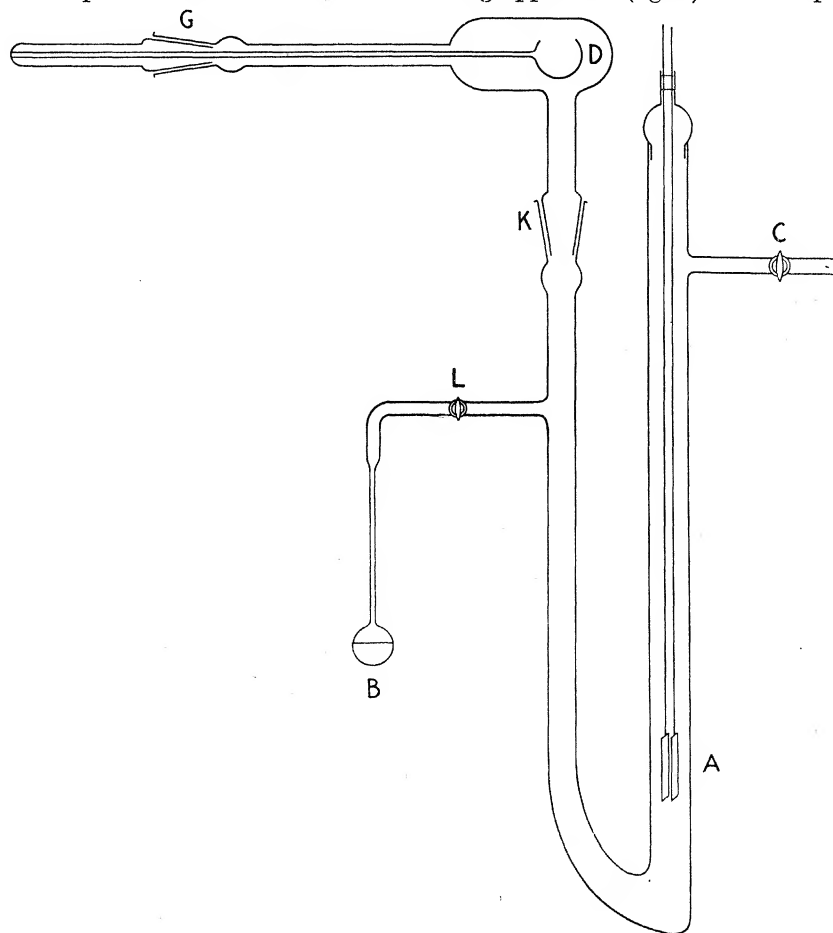

Fig. 2.

* Willows, 'Phil. Mag.,' (6), vol. 24, p. 891 (1912).

were investigated in the tube A (12 mm. diameter), which was connected through the tap C with a manometer, pump and charcoal tube. The salt was placed at the bottom of the tube and at a distance of 4 cm. two platinum plates were fixed (1·5 sq. cm. surface, distance between the plates = 0·5 cm.). One of the plates was connected to a Wilson electroscope (12·5 divisions per volt) and the second kept at the potential − 200 volts. Preliminary experiments showed that, for the same potential difference, the current obtained was much smaller when the potential was applied for a long time than in the case when the electrode was charged only during the measurements. Therefore, to keep the conditions steady, the plate was always connected with one pole of the storage cells. The water was placed in a small bulb B separated from the main apparatus by the tap L. (The upper part K was not used in this experiment.) The lower end of the apparatus was placed in the electric furnace. To free the bulb of air the water was frozen with liquid air and the whole apparatus exhausted with charcoal. The stopcock L was then turned on and the ice allowed to melt.

At first an experiment was made in order to test whether the presence of the water vapour had any action on the insulation. For that purpose the empty apparatus was exhausted and heated up to about 280° C., then the stopcock C was closed and L opened. The observations showed that after about 15 minutes a small conductivity over the surface of the insulation appeared, but in any case this current was negligibly small in comparison with that which was obtained when the tube was filled with salt vapour.

The influence of water was tested for the salts cadmium iodide, zinc bromide, zinc iodide, potassium chloride, and potassium iodide, and the results obtained are set out in Table I, p. 638.

In the case of cadmium iodide 1 grm. was used and the apparatus exhausted to 10^{-4} mm. of mercury and heated up to 264° C. In the case of zinc bromide 1 grm. of the salt was placed in apparatus and kept one day in charcoal vacuum to liberate all water vapour, which is known to be very easily absorbed by this substance. The pressure was $1·6 . 10^{-2}$ mm. and the temperature 295° C.

For zinc iodide 0·3 grm. was dried four days in a charcoal vacuum. The temperature was 270° C., and the pressure at the beginning of the observations was $3 . 10^{-5}$ mm. All the salts were obtained from Kahlbaum.

As may be seen from the Table I water vapour has a very marked influence on the current passing in the salt vapours. The greatest increase of the conductivity was observed in the case of zinc iodide, which is also the most hygroscopic substance of those investigated. The curious point is that the greatest conductivity is observed when the reservoir with the water is cut

Table I.

Cadmium iodide.		Zinc bromide.		Zinc iodide.	
Time.	*Current.	Time.	Current.	Time.	Current.
min.		min.		min.	min.
0	19·8	0	64·5	0	24·1
6·8	19·4	3	52·6	11	22·7
7·3	L opened	L opened, C closed		L and C opened	
	C closed	4·7	182	13	60·6
9·3	29·0	9	250	L opened, C closed	
13·3	38·1	L closed, C opened		19	200
18	43·5	11	333	22	213
18·5	L closed	13	200	L closed, C opened	
	C opened	17	182	24·5	286
19·8	37·7	21·5	143	28·8	400
25·3	30·8	Again L opened		48·8	32·3
31·8	30·3	C closed		Again L opened	
		30·5	167	C closed	
		33	200	56·5	105
		38	222	L closed, C opened	
		L closed, C opened		67	62·5
		39·2	250		
		43	117		

* Arbitrary units.

off and the water vapour begins to get absorbed by the charcoal and phosphorus pentoxide. This phenomenon may be due to the fact that the conductivity of the salt vapours depends not only on the presence of the water, but also on the pressure of the gas filling the apparatus. It was shown by Schmidt that increase of pressure diminishes the current. It may therefore be expected that the rapid absorption of water vapour will be accompanied by an increase of the current.

Of the salts which do not show any conductivity when heated, potassium chloride and potassium iodide were tested. It was especially interesting to test the influence of water vapour on the last substance, as H. A. Wilson* observed a large current when a solution of KI was sprayed into a hot platinum tube (270° C.). Garrett, however, noticed no leak when the dry salt was heated to the same temperature. The experiments with this substance were carried out with a somewhat different arrangement. The Wilson electroscope was replaced by a quadrant electrometer giving 50 divisions per volt. The water vapour was absorbed by a tube immersed in solid carbon dioxide, and for measuring the current a small cylindrical condenser was used instead of the two platinum plates; 3 grm. of KI were placed in the tube A and heated for two hours at a temperature of 308° C. The apparatus was exhausted with a Gaede pump to 10^{-4} mm.

* H. A. Wilson, 'Phil. Trans.,' A, vol. 197, p. 415 (1901).

The outer tube of the condenser was charged to +100 volts, and the inner was connected with the electrometer. At the commencement of heating a small leak was observed, which did not persist long, however, and the electrometer became perfectly steady. When the stopcocks L and C were opened and a stream of water vapour was admitted into the tube A a considerable deflection was noticed (five divisions in 10 seconds). When the stopcock L was closed the current disappeared also. The phenomenon was repeated several times with identical results.

Potassium chloride was tested in the previous arrangement (with the Wilson electroscope); when the dry salt was heated to the temperature 303° C. at a pressure about 10^{-4} mm. no current was observed as in the case of KI. In the first moment when the water vapour was admitted the gold leaf showed a small and irregular movement; this current, however, diminished gradually, and in a few minutes the water did not produce any leak. Very likely the initial increase was also due to some secondary effect.

Change of Conductivity with the Time.

This question has been the subject of many investigations. Garrett has shown that the conductivity produced by heated salts increases for about 20 minutes up to a certain maximum and then begins to fall. The relation between the current and the time was found to be expressed by the formula

$$i = A\,(e^{-\lambda_2 t} - e^{-\lambda_1 t}),$$

where A, λ_1, and λ_2 are constants. In his last paper Schmidt suggested the idea that the decrease of conductivity is due to two factors: (1) to the diminution of the surface of the salt during the heating, and (2) the change of concentration of ions due to their removal by the electric field.

The experiments described in the previous paragraph show that the water vapour has enormous influence on the current passing in the salt vapours. It was interesting, therefore, to test if the initial stage of conductivity is not also complicated by water vapour, which is usually absorbed by the salts and liberated during the heating. For that purpose some measurements were made in conditions when all possible care was taken to get rid of traces of water vapour present in the apparatus. Cadmium iodide was used for this, as it does not contain any water of crystallisation, and therefore one can remove the water vapour absorbed by the salt by careful drying *in vacuo*. The apparatus described in the previous paragraph was used for the measurements. To have a supply of the dry air the bulb B was replaced by a larger reservoir, in which the air could be kept in presence of phosphorus pentoxide. To follow in more detail the initial stage of

conductivity, the salt was not heated together with the tube A, but it was placed in a small glass spoon D, whence it could be thrown into the apparatus by turning the ground glass connection G. Two sets of measurements were made with cadmium iodide—

1. The salt was placed into the spoon D, the apparatus was exhausted to 0·75 mm. and immediately heated.

2. The apparatus with cadmium iodide in the spoon D was exhausted with charcoal to about 10^{-3} mm. and kept at that pressure for about five hours. The apparatus was then filled with air which had remained a few days in contact with phosphorus pentoxide. By opening the charcoal tube the pressure was then reduced to 0·51 mm. The readings obtained in both cases are given in Table II and in the diagram, fig. 3.

Table II.

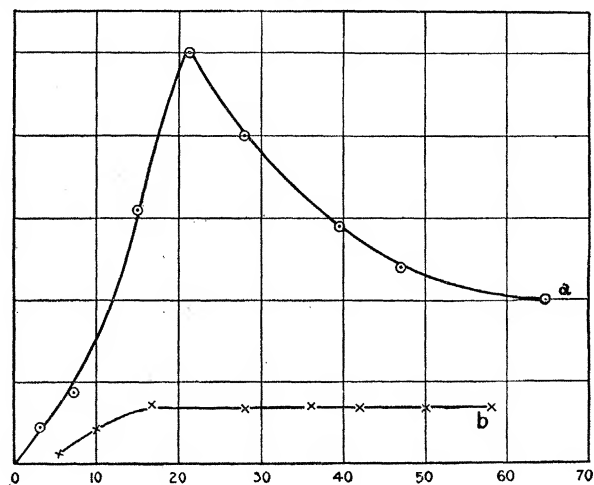| Not dried; temperature = 271° C.			Dried; temperature = 285° C.		
Time.	Current.	Pressure.	Time.	Current.	Pressure.
min.			min.		
0·0	Salt thrown down	0·74	0·0	Salt thrown down	0·51
3·1	4·5	0·9	5·5	1·25	Constant
7·2	8·7	—	10·0	4·2	
9·5	—	0·82	16·7	7·1	
12·5	31·0	0·79	28·0	6·7	
21·3	50·0	0·765	36·0	7·0	
28·0	40·0	0·76	42·0	6·7	
39·5	29·0	0·75	50·0	6·7	
47·0	24·0	—	58·0	6·7	
65·0	20·0	0·75			

FIG. 3.

The curve obtained in the first case (fig. 3, *a*) does not differ from those obtained by the previous investigators if we take into account that the initial increase is due to the heating of the salt and to the diffusion of the vapours to the upper parts of the tube. On the contrary, the current obtained with dry salt and dry air is practically constant. It is interesting to note that, although cadmium iodide is not supposed to be very hygroscopic, nevertheless it liberates during the heating a considerable amount of water vapour, as will be seen from the change of pressure during the experiment. In a few minutes after throwing the salt into the tube A the pressure increased from 0·74 to 0·9. After that it began to decrease, and after about half-an-hour reached its initial value.

Further experiments with cadmium iodide were carried out in a high vacuum obtained by the cooled charcoal method. It was expected that when the salt remained for a longer time in a very high vacuum and the gases liberated during the heating were instantly removed, the current passing through the salt vapours would be more constant. For this experiment 1 grm. of cadmium iodide was kept for one day in the highest vacuum obtained by charcoal, the apparatus was then heated and the salt thrown down. The readings obtained are shown in Table III and fig. 4.

During the last experiment the charcoal tube was open all the time and

Table III.

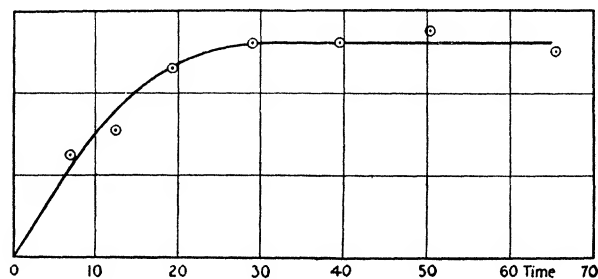| Time.	Temperature.	Current.
min.	°	
7·0	267·0	25
12·5	267·0	31
19·3	267·5	46
29·0	268·0	52
39·5	268·0	52
50·5	269·0	55
65·5	268·0	50

Fig. 4.

the pressure of air remaining in the apparatus was about 3×10^{-5} mm. The electrode was charged the whole time to -200 volts. The furnace was heated by the main battery of the laboratory and it was difficult to keep the temperature of the apparatus more constant. We may therefore regard the currents obtained after 20 minutes' heating as practically constant.

Thus in the case of cadmium iodide it seems possible to obtain a fairly steady current in the vapours when the salt is properly dried. Similar experiments were made with zinc iodide and zinc bromide, but the influence of drying was not expressed so distinctly as in the previous case. It may be that such a definite result could be obtained with cadmium iodide because this salt is not very easily volatilised and the change of conductivity due to the diminution of the surface of salt does not play a very great *rôle*.

Influence of Temperature.

The influence of change of temperature on the conductivity produced by heated salts was tested by Garrett and by Schmidt. In Garrett's experiments the salt was placed on one of the plates of the condenser and heated by an electric furnace surrounding the whole. Thus, the current passing between the plates was due to the emission of the charges from the surface of the hot salt and to the conductivity of vapours. The component of the current due to the conductivity of vapours was complicated by the change of pressure of the salt vapours. Garrett observed that the current varied with the temperature according to Richardson's law, and it therefore appears probable that in these conditions the thermionic effect of the salt plays the chief *rôle*. Further measurements of the temperature effect were made by Schmidt, who observed that the conductivity increases with temperature, at first slowly and then more rapidly. Schmidt's arrangement allowed the conductivity of the vapours to be measured. However, in his experiments also the constancy of the pressure was not taken into account and therefore the rapid increase of the current might have been due to the change of density of the vapours.

The following set of measurements was made in the conditions where the temperature of the vapours could be varied independently of the temperature of the salt.

Two grammes of cadmium iodide were placed on the bottom of a glass tube (about 1·7 cm. diameter) and heated in the electrical furnace to 209° C. At the distance of about 20 cm. a cylindrical condenser was placed, consisting of a platinum tube 10 cm. long and 2 cm. in diameter, in the centre of which was fixed a narrow platinum tube 2 cm. long and 2 mm. in diameter. The outer electrode was charged to -200 volts and the inner one connected to a Wilson electroscope. The upper part of the tube was surrounded by a second

electrical furnace in such a way that the vapour passed a distance of about 15 cm. in it before reaching the condenser so as to acquire the temperature of the second furnace. The whole apparatus was exhausted and the salt was kept for one day in a charcoal vacuum. During the experiment the pressure was 6×10^{-5} mm. In Table IV the measurements of the current at the various temperatures are given. It was found that the logarithms of the current are in a linear relation with the reciprocals of the absolute temperatures of the vapours (see fig. 5, A). Therefore the connection between the current i and the absolute temperature ϑ may be expressed in the following form

$$i = ae^{-b/\vartheta}, \tag{1}$$

where a and b are constants. In the top column of Table IV the absolute temperatures calculated according to the formula

$$i = 10^{21\cdot3} e^{-2\cdot35 \times 10^4/\vartheta}$$

are given. The agreement with experiment is fairly satisfactory.

Table IV.

Absolute temperature of vapours—							
Calculated	487	502	511	522	532	550	562·5
Observed	486	499	511	523	533	548	560
Current in arbitrary units	2·78	10·5	21·5	54·6	129	575	1450

To follow the connection between the current and the temperature over longer intervals some modifications were made in the previous arrangement. The tube containing the salt was made of fused quartz (diameter 1 cm.) placed horizontally and joined to the apparatus by sealing wax cooled by a copper jacket. For measuring the temperature of the furnace an iron-constantan thermo-couple was used. It was mentioned above that the electrodes placed in the vapours were connected continuously with the source of potential to secure greater constancy of readings. As the increase of temperature produces a new concentration of ions it was necessary after obtaining the steady temperature to wait a certain time until the equilibrium was reached. As this process goes fairly slowly it was not possible to take readings at many temperatures, otherwise the conditions would not be identical. The results obtained in this arrangement with ZnI_2, $ZnBr_2$, and CdI_2 are to be seen in the Table V or on the diagram, fig. 5.

The discrepancy between the calculated and observed temperatures is somewhat greater in this case than in the previous one. This disagreement may be due to the variation of pressure of the salt vapours during the experiment,

Table V.

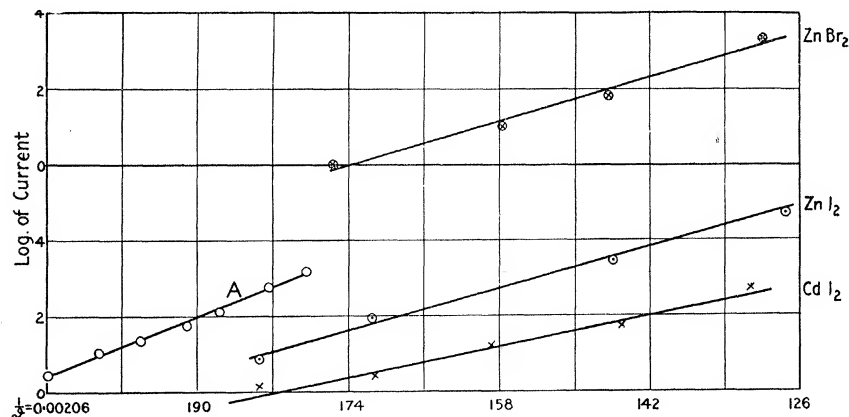| Zinc iodide. Temperature of salt, 267° C.			Zinc bromide. Temperature of salt, 271° C.			Cadmium iodide. Temperature of salt, 256° C.		
Current.	Absolute temperature.		Current.	Absolute temperature.		Current.	Absolute temperature.	
	Observed.	Calcu-lated.		Observed.	Calcu-lated.		Observed.	Calcu-lated.
7·4	545	541	1·0	570	578	1·4	545	555
83·3	583	591	10·0	635	627	2·63	583	573
625·0	633	638	62·5	683	671	16·7	629	631
2778·0	684	679	2270·0	766	777	55·6	689	677
50000·0	784	777				556·0	761	784

FIG. 5.

which takes a considerable length of time (about 3 hours). Anyhow the linear connection between $\log i$ and $1/\vartheta$ may be accepted as a first approximation. The following formulæ were used for calculation of absolute temperatures in the above Table :—

$$\mathrm{ZnI_2}: i = 10^{13\cdot47}e^{-1\cdot57\times10^4/\vartheta}; \qquad \mathrm{ZnBr}: i = 10^{13\cdot05}e^{-1\cdot74\times10^4/\vartheta};$$

$$\mathrm{CdI_2}: i = 10^{9\cdot05}e^{-1\cdot14\times10^4/\vartheta}.$$

In the previous experiments it was shown that the conductivity in the salt vapours is mostly due to the processes which are going on in the vapours themselves. The question now arises whether the observed conductivity is due to the volume ionisation of the vapours or to the chemical action of vapours on the platinum electrodes. An attempt was made to decide this point. The tube, with a sample of cadmium iodide, was

placed horizontally, and the current passing between the plates was measured. One of the electrodes was then removed and covered with spongy platinum powder, so that its surface was greatly increased, while the volume of the vapour between the plates remained practically constant. Therefore, if the observed ionisation was due to the surface effect, it might have been expected that the current would be much stronger than in the previous case. However, the results showed that the current obtained with the spongy platinum electrode was of the same order as in the previous case, consequently this experiment seems to show that the conductivity is chiefly due to the volume ionisation.

If we assume that the conductivity of vapours is due to their electrical dissociation, we may easily calculate the work required to ionise one molecule of vapour, applying the formula of van't Hoff*

$$\frac{q}{2}\left(\frac{1}{T_2} \quad \frac{1}{T_1}\right) = \log \frac{x_1^2}{x_2^2} \cdot \frac{T_2}{T_1},$$

where q is number of calories required to dissociate one gramme-molecular weight of vapours, x_1 and x_2 are ratios between the number of dissociated and neutral molecules at the temperatures T_1 and T_2. Calculating in this way the energy required to ionise one gramme-molecular weight of vapours and dividing it by the number of coulombs required to electrolyse one gramme-equivalent weight of any substance, we obtain the following values for the ionising potential of different salt vapours:—

	q.	w (volts).
Cadmium iodide	$4{\cdot}4 \times 10^4$	$1{\cdot}93$
Zinc iodide	$6{\cdot}2 \times 10^4$	$2{\cdot}72$
Zinc bromide	$6{\cdot}8 \times 10^4$	$2{\cdot}97$

These values are much less than the corresponding potentials for gases.

Ionisation and Dissociation.

It is known that the salt vapours studied in the foregoing experiments are easily decomposed. It seemed interesting, therefore, to test other substances the vapours of which are dissociated at high temperatures. For that purpose phosphorus pentabromide and sulphur dichloride were tried. The first compound is dissociated at 100° C. and the second at 64° C. The experiments were carried out in two different arrangements. The first apparatus consisted of a small tube with two platinum electrodes, one of which was charged to 100 volts, and the second connected with a quadrant electrometer. A small bead of phosphorus pentabromide was placed inside

* H. A. Wilson, 'Phil. Trans.,' A, vol. 197, p. 415 (1901).

the tube, which was then exhausted with a Gaede pump and sealed off. The tube was placed in an oven, which could be heated with a Bunsen
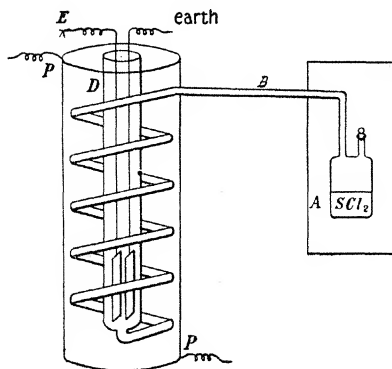

FIG. 6.

burner. In the second arrangement the substance was placed in the small vessel A (fig. 6), which was placed in an oven, the temperature of which could be regulated. The vapours emerged through the tube B, passed through the spiral, and came into the tube D, in which were placed two electrodes, one of them earthed, and the second connected with the electroscope, charged to about 300 volts. The spiral and the tube D were placed in the electric furnace, so that the temperature of the vapour could be varied without changing the temperature of the substance itself.

The experiments carried out with both arrangements have shown that the vapours of the above-mentioned substances do not conduct the electric current when they are dissociated by heat. This negative result shows that the dissociation cannot be regarded as the cause of the ionisation.

*Summary.**

The experiments described show—

1. The conductivity of the salt vapours is due to the processes occurring in the vapours themselves.

2. The vapours of carefully dried salts conduct the electric current. Therefore the conductivity cannot be ascribed to the chemical action of water vapour on the salt vapours. However, the presence of water vapour increases the current passing in salt vapours.

3. When cadmium iodide was very carefully dried, it was possible to observe a current which was practically independent of time.

4. The connection between the current i and the temperature ϑ may be expressed with considerable accuracy by the formula

$$i = ae^{-b/\vartheta},$$

where a and b are constants.

5. The ionising potential calculated from the energy of dissociation is considerably less than that for the ordinary gases.

6. The dissociation of vapours is not always accompanied by ionisation.